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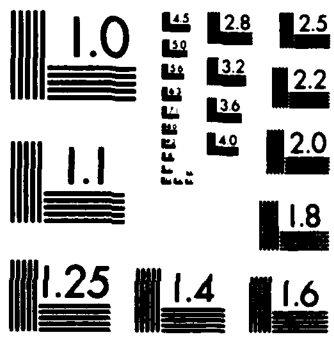
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FOREIGN TECHNOLOGY DIVISION

INVESTIGATION OF THE ROTATION OF MOLECULAR GROUPS IN POLYMERS OF METHYL ACRYLATE AND VINYL ACETATE BY THE METHOD OF IR-SPECTROSCOPY

by

O.N. Trapeznikova, T.V. Belopol'skaya

HUMAN TRANSLATION

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О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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INVESTIGATION OF THE ROTATION OF MOLECULAR GROUPS IN POLYMERS OF METHYL ACRYLATE AND VINYL ACETATE BY THE METHOD OF IR-SPECTROSCOPY

O.N. Trapeznikova, T.V. Belopol'skaya

Physics Institute of Leningrad State University
im. A.A. Zhdanov
Submitted 17 July 1967

In this paper results are given from measurements of the IR-spectra of absorption of polymethyl acrylate (PMA) and polyvinyl acetate (PVA) in the range of frequencies of 1100-1400 cm^{-1} at temperatures of 77 and 295°K.

The infrared spectra of absorption of PMA and PVA at room temperature were obtained and analyzed by a number of authors [1, 2]. The investigated range of frequencies corresponds to C--O stretching vibrations.

Earlier we investigated the spectrum of absorption of polymethyl methacrylate (PMMA) in the same range of frequencies at temperatures of 66, 77 and 295°K [3]. It was shown that the total intensive band of 1100-1300 cm^{-1} consists of five components and an interconnection exists between two of the components, namely: an increase in the integral intensity of the band at 1197 cm^{-1} takes place at the expense of a lessening of intensity of the band at 1172 cm^{-1}. This gave us a basis for concluding that these bands are conditioned by the presence of two isomer states and are related to rotational isomerism inside the ester group. The band at 1197 cm^{-1} is related to the more stable, and the band with a maximum at 1172 cm^{-1} to the less stable state. At 67°K the band at 1172 cm^{-1} almost disappears, which indicates the freezing of the corresponding isomer with a lowering of temperature.

Analagous conclusions were made by us on the basis of measurements of the temperature dependence of birefringence of PMMA at low temperatures. The change of birefringence at temperatures above 40°K we connected with a change in the anisotropy of polarizability of the ester group and we explained it by the transition of this group from the cis-configuration, which is more stable at low temperatures, into

the trans-configuration, which is realized by the rotation of O--CH_3 around the C--O bond by 60°.

PMA differs from PMMA only by the absence of a side methyl group in the chain of the main valencies. In PMA this group is replaced by an atom of hydrogen. In this case also the temperature dependence of birefringence of PMA at low temperatures indicates the excitation of rotational isomerism above 40°K, although this dependence in PMA is expressed less distinctly than in PMMA [5]. The lesser change in the polarizability of the ester group of PMA in the case of a great degree of freedom of rotation was explained by us by the turning of the group by 160°, since it is easy to show (accepting the additivity of polarizability) that with the rotation of the O—CH_3 group by 180° the anisotropy of polarizability of the ester group is not changed. As far as the dipole moment of the ester group is concerned, then it is changed, and in this case the C--O bond in the O—CH_3 group will interact with the C—C bond. This circumstance may be reflected in the position of the absorption band of the second isomer of PMA in comparison with PMMA.

Polyvinyl acetate is a structural isomer of polymethyl acrylate, and one of the two individual C—O bonds of the PVA connects the side acetate group with the carbon chain. In PVA, in contrast to PMMA and PMA, the rotation around both C-O bonds can change the anisotropy of polarizability. As shown by the measurements of the temperature dependence of birefringence right up to 20°K [5], there is no rotational isomerism in PVA. The insignificant change in birefringence with temperature has a different nature than in the cases of PMA and PMMA, and can be explained by the excitation of torsional vibrations in the acetate group.

RESULTS

Figures 1 and 2 show the spectra of absorption of PMA and PVA measured by us at 77 and 295° in the area of frequencies from 1100 to 1400 cm^{-1}. The experimental method used is analogous to that described earlier [6]. As is evident from Figure 1, in PMA there is a band of absorption which is analogous to the band in PMMA. It has four clearly expressed maxima, and a lowering of temperature, just as in PMMA, leads to an increase of the 1197 cm^{-1} band. It can be noted that with a lowering of temperature there is an overall increase in the intensity

of the bands of absorption and there shifting by 3-5 cm^{-1} to the side of higher frequencies.

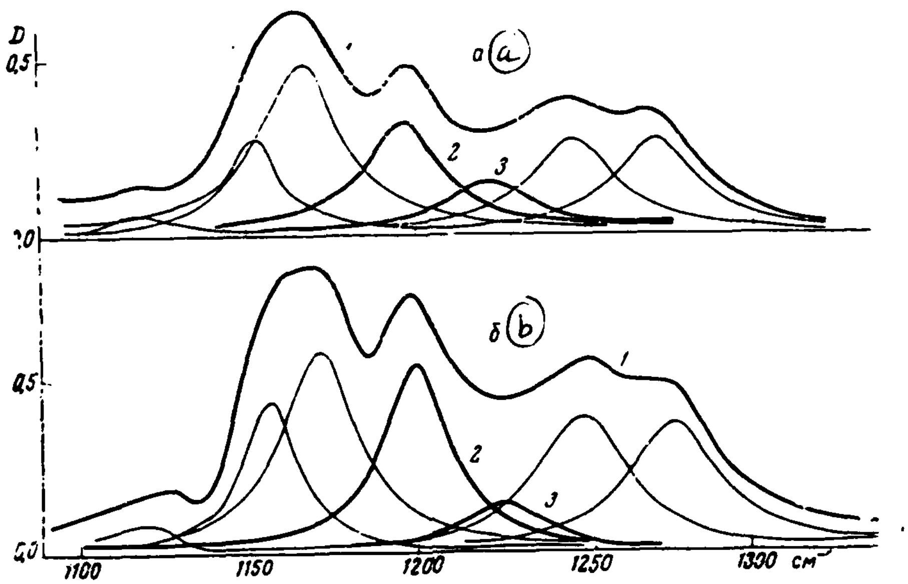

Figure 1. Breakdown into component bands of absorption of PMA in the area of frequencies of 1100-1350 cm^{-1} at 295 (a) and 77°K (b): 1 - experimental total curve, 2, 3 - component bands, belonging to isomeric states of the ester group.

This total band was broken down into components, stemming from the assumption that the contour of the band of absorption is described by a dispersion formula. We found its structure somewhat different from the band for PMMA. In PMA this band consists of six components, two of them are interconnected - these are the bands of 1197 and 1223 cm^{-1}. With a lowering of temperature the integral intensity of the 1197 cm^{-1} band increases as much as the integral intensity of the 1223 cm^{-1} band decreases. Thus in this case also we observe the appearance of rotational isomerism in the ester group, and the 1197 cm^{-1} band, just as in PMMA, belongs to the more stable isomer. However, in the case of

PMA the band of absorption which corresponds to the less stable isomer (1223 cm^{-1}) is shifted with respect to the 1197 cm^{-1} band to the side of greater frequencies by 26 cm^{-1} (in PMMA by 25 cm^{-1} to the side of lower frequencies). The 1223 cm^{-1} band is less active than the 1172 cm^{-1} band in PMMA. This may be connected with the fact that in the case of the proposed turning of the group by 160° the C--O bond in the O—CH_3 group will interact primarily with the C—C bond, and not with C=O.

The difference in energies of the isomer states of the ester group, calculated using the spectral data obtained. is equal to approximately 120 cal/mole. This magnitude of difference in energies is less than in PMMA, which conforms to the fact that in PMA a greater freedom of rotation is realized inside the ester group.

As far as the 1250 and 1277 cm^{-1} bands are concerned, their intensity (within the limits of error) changes with a lowering of temperature in accordance with an overall increase in the intensity of all the bands. They are analogous to the same bands in PMMA, and their nature is still unexplained. At the present time we also cannot point out the origin of the band with the maximum of 1157 cm^{-1}, we can only note that it is not in the spectrum of the polymer of methyl methacrylate, but it is present in the spectrum of its monomer at low temperatures [7].

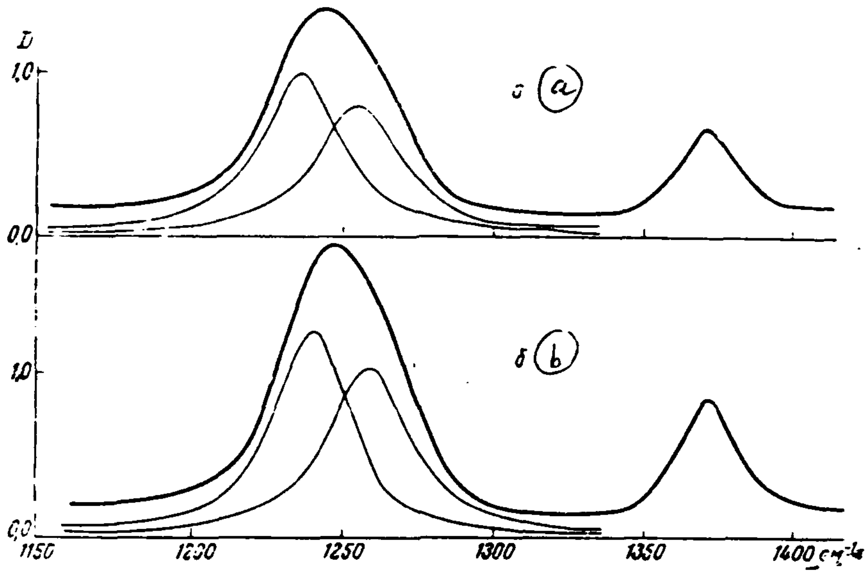

Figure 2. Breakdown into component bands of absorption of PVA in the range of frequencies of 1150-1330 cm^{-1} at 295 (a) and 77°K (b).

In the absorption spectrum of PVA, which is depicted in Fig. 2,a, there are two bands of absorption with frequencies with maximums at 1245 and 1375 cm^{-1}. Different authors connect the 1245 cm^{-1} band with selective vibrations of the acetate group, and the 1375 cm^{-1} band with symmetric deformation vibrations of the methyl groups [1, 2]. With a lowering of temperature from 295 to 77° the contour of the 1245 cm^{-1} band remains almost the same. Thus in the investigated area of the spectrum of PVA there are no such changes which would indicate the existence of rotational isomerism in the acetate group, which is found in complete conformity with the conclusions made on the basis of the temperature dependence of birefringence of PVA.

It should be noted that in PVA the investigated absorption band is very intensive and wide in comparison with the bands of PMA, and it

is also somewhat asymmetric. We propose that this band is a composite and consists of two bands which change with temperature in the same manner. Figure 2 shows the separation of the band into two components with frequencies of the maxima at 1237 and 1256 cm^{-1}, and the ratio of the integral intensities of these maxima remain constant with a lowering of temperature. We consider it possible to relate them to the stretching vibrations of two individual C-O bonds. However, this assumption does not agree with the interpretation of the authors of work [2], who investigated dichroism of the main bands of absorption in the spectrum of PVA, where the 1245 cm^{-1} band is attributed to the stretching vibration of the C-O bond which enters into the composition of the acetate group, and the 1025 cm^{-1} band - to the stretching vibration of the second C-O bond. However, in comparing the IR-spectra of absorption of PMMA, PMA and PVA in the range of frequencies under consideration, it can be seen that in the case of PMMA and PMA, where rotational isomerism exists inside the side group, there are three components, and in the case of PVA, where there is no rotational isomerism, there are only two components, which confirms the correctness of referring the bands to PVA, which we proposed.

CONCLUSIONS

Absorption spectra are given for polymethyl acrylate and polyvinyl acetate in the areas of C—O stretching vibrations, measured at 77 and 295°K. In the range of frequencies of 1100-1300/cm^{-1} a wide intensive band of absorption is found, the contour of which changes with temperature. Following the separation of this band into components

(there turned out to be six) and comparing the behavior of the individual components when the temperature is changed, a conclusion was made concerning the presence in polymethyl acrylate of rotational isomerism in the ester group. In polyninyl acetate in the same range of frequencies there is one wide band of absorption, the contour of which does not change with a change of temperature. (Russian Translation)

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